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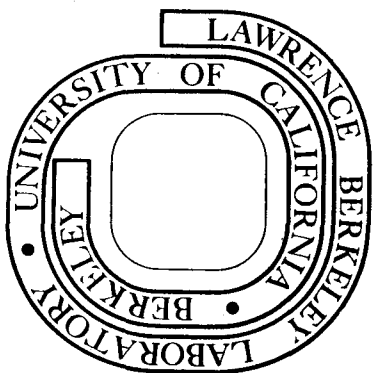
L. L. Kesmodel, P. C. Stair, and G. A. Somorjai

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On the Relaxation of the Pt(111) Surface:
Results of Dynamical LEED Calculations

by

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The technique of low-energy electron diffraction (LEED) intensity-voltage (I-V) analysis has found increasing application in recent years to quantitative study of the atomic structure of solid surfaces [1]. In particular, if dynamical diffraction is properly considered, one may employ I-V analysis to determine the outward or inward geometric relaxation that may occur at the surface of a crystal relative to the bulk interlayer spacing. For the case of relaxation, (as opposed to reconstruction) the two-dimensional (x,y) unit cell parallel to the surface that is given by the appropriate termination of the bulk lattice is preserved and one has, in the simplest case, a small expansion or contraction in the z-distance between the first and second surface layers.

We carried out such a LEED study a few years ago for the clean Pt(111) surface at room temperature and found that the relaxation was less than $\pm 5\%$ of the bulk spacing [2]. Due to limitations of the computational method used at that time, the energy range was restricted to $E \leq 100$ eV and relaxations of more than $\pm 5\%$ were not considered. However, in a recent preliminary study using ion channeling/backscattering techniques [3], it has been suggested that the Pt(111) surface may be outwardly relaxed by

15%, corresponding to a very sizable displacement of 0.31 \AA . Unfortunately, definitive comparison with our earlier conclusions was precluded by apparent surface contamination in the ion-channeling experiments [3].

It is obviously of both experimental and theoretical interest to determine an accurate value for the surface relaxation. To this end, we report here more extensive calculations using dynamical LEED theory which confirm our original conclusion [2] and strongly argue that the relaxation is indeed less than a few percent.

In the dynamical LEED calculations reported herein, a beam representation of the scattering from a given atomic layer was employed, and the efficient layer-doubling method [4] was used to combine layers; this approach is exact providing a sufficient number of evanescent waves are retained in the interlayer scattering summations. The beam representation with layer-doubling is numerically equivalent to but computationally much more efficient than the approach used earlier involving Beeby's matrix inversion theory [2]. For this reason we were able to extend the calculation to 180 eV using 8 partial-wave scattering phase shifts and to consider the possibility of outer-layer relaxations of up to $\pm 20\%$. The muffin-tin model potential and other non-structural parameters describing the Pt scattering were the same as those used in Ref. 2 with the exception of the imaginary component of the potential. The value of 2.5 eV for this damping parameter gives a better description of fine structure in the I-V profiles than the previously used value of 4.0 eV.

The results of these calculations are briefly illustrated for the purposes of this letter in Figs. 1-3 for three non-specular diffraction beams

at an incidence angle of $\theta = 16^\circ$. These figures are completely representative of the results obtained for other beams at $\theta = 16^\circ$ as well as results for six beams at $\theta = 4^\circ$. Comparison was made to some 50 major experimental peak positions as well as analysis of minor shoulder peaks, relative intensities, and line shapes. The analysis from 100-180 eV is particularly relevant since this region is less affected by uncertainties in non-structural parameters than the region below 100 eV. The experimental data were obtained as previously reported using the rapid photographic collection method with automated scanning [5] and were extended to 200 eV [6]. It is clear from Figs. 1-3 that the LEED I-V profiles are sensitive to a small outer-layer relaxation and that the dynamical theory gives a quite satisfactory description of experiment for the very small (0%, $\pm 2.5\%$) relaxations. A relaxation of +15% suggested by the ion-channeling experiments [3] is obviously ruled out, and even relaxations of $\pm 5\%$ are relatively unfavorable upon close inspection of peak positions, line shapes, and relative intensities. Although a few small discrepancies between theory and experiment inevitably remain, all our evidence indicates that forces at the Pt(111) surface combine in such a way as to give a very small ($\lesssim 2.5\%$) relaxation of the outermost layer of atoms. We should also mention that with the adsorption of a one-fourth monolayer coverage of acetylene no major changes in the integral-order beam intensities above 100 eV, aside from attenuation, are found. This indicates that in this case, impurity adsorption does not lead to a relaxation of the topmost layer of Pt atoms [7].

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Figure Captions

- Fig. 1. Comparison of calculated (solid lines) and experimental (dotted line) I-V profiles [$(\bar{2}0)$ beam] for a range of expanded (+) and contracted (-) values of the distance between the first and second atomic layers relative to the bulk spacing. A relaxation of 10% corresponds to a displacement of 0.2 \AA .
- Fig. 2. Comparison of calculated and experimental I-V profiles for the $(0\bar{1})$ beam. Other conditions as in Fig. 1.
- Fig. 3. Comparison of calculated and experimental I-V profiles for the $(\bar{1}\bar{1})$ beam. Other conditions as in Fig. 1.

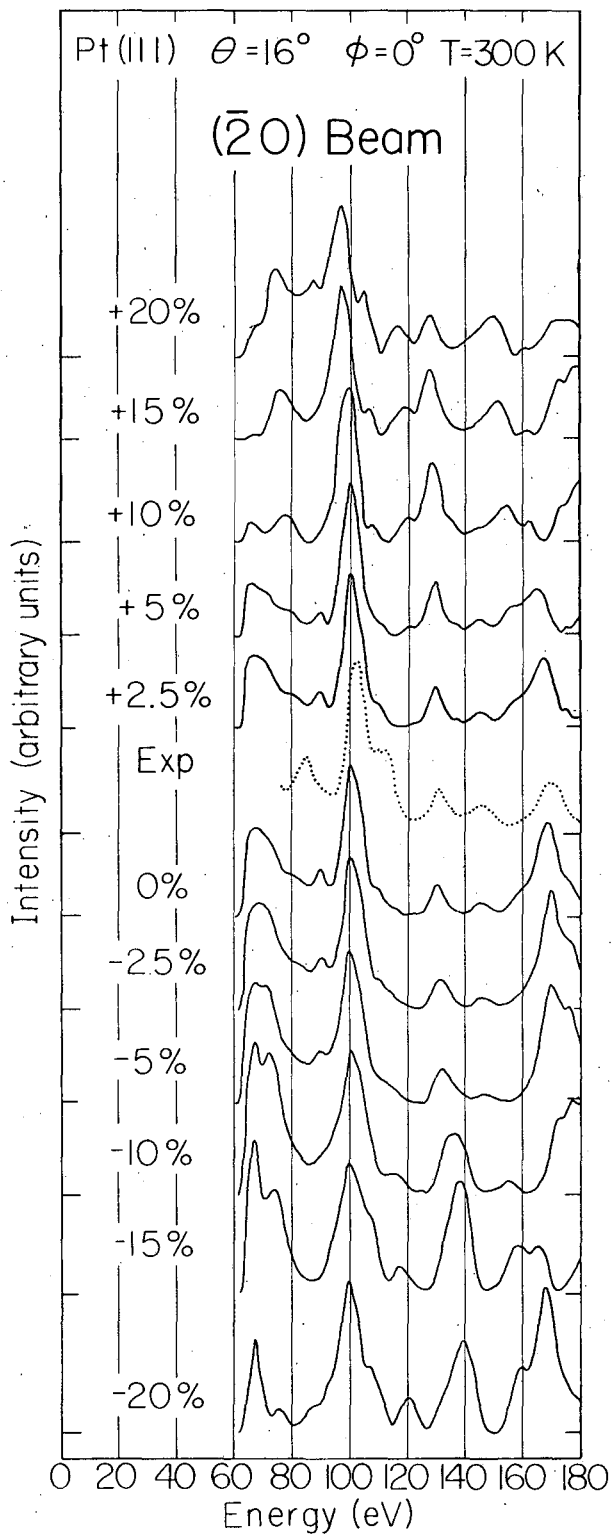
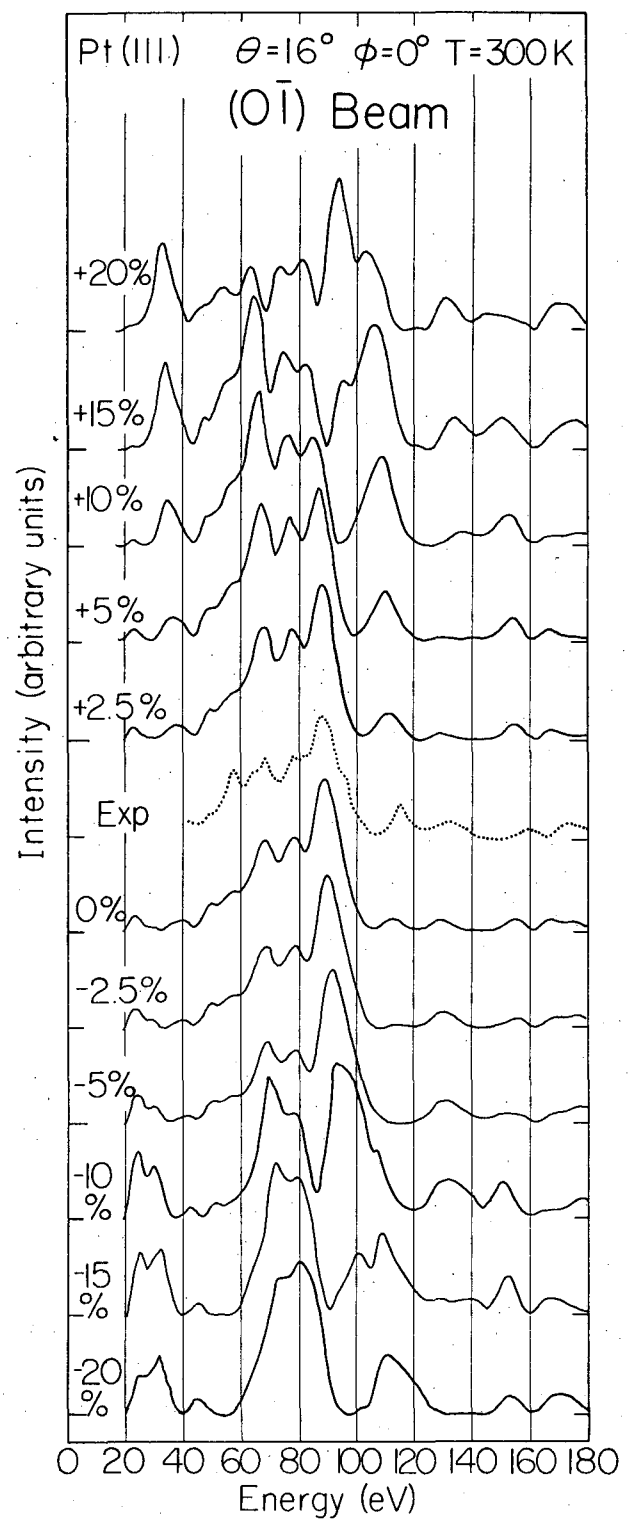


Fig. 1



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Fig. 2

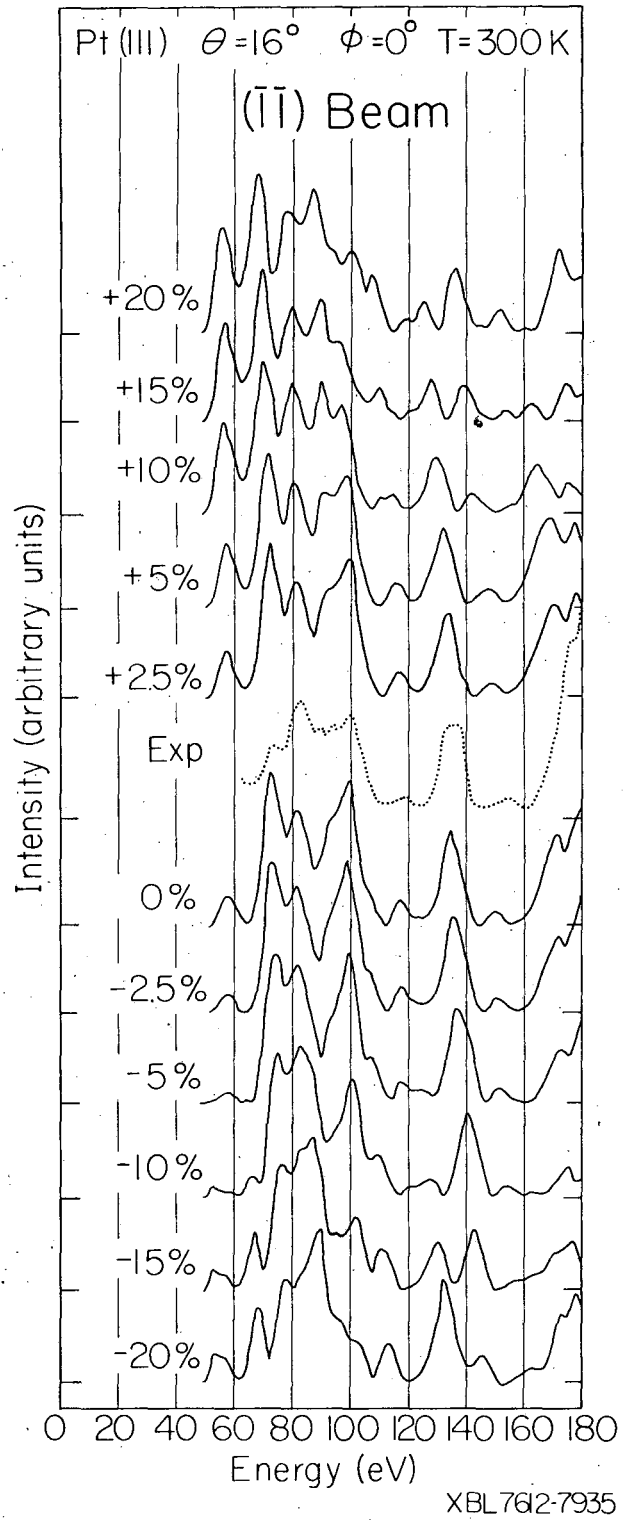


Fig. 3

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